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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53(c).

TITLE: BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION

Inventor(s)/Applicant(s):

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☒ 14 pages of specification are enclosed.

☒ 1 sheet(s) of drawings are enclosed.

☒ Small entity status is claimed for this application.

☒ Provisional Filing Fee Amount:
☐ $160, large entity
☒ $ 80, small entity

☒ A check in the amount of $80.00 to cover the filing fee is enclosed.

☒ The Director is hereby authorized to charge any additional fees which may be required in connection with the filing of this provisional application and recording any assignment filed herewith, or credit over-payment, to Account No. 02-4550. A copy of this sheet is enclosed.

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BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION

FIELD

This disclosure concerns nonlinear optical materials and devices employing such materials.

BACKGROUND

Nonlinear optical (NLO) materials are unusual in that their optical properties are affected by light. For instance, light polarizes certain materials. If the polarization is linear, then light emitted by the material has the same frequency as the absorbed light. NLO materials are polarized in a nonlinear manner. As a result, the frequency of the light emitted by a nonlinear optical material is some value times the frequency of the light incident on the material.

Certain compounds belonging to the same series as materials of the present disclosure appear to be taught by the Russian-language publication: Disordered structures of rare earth scandoborates of the huntite family. Kuz'micheva, G. M.; Rybakov, V. B.; Novikov, S. G.; Ageev, A. Yu; Kutovoi, S. A.; Kuz'min, O. V. Zhurnal Neorganicheskoi Khimii (1999), 44(3), 352-366. This publication is incorporated herein by reference.

Laser technology is one field that has benefited from the development of new NLO materials. Known NLO materials generally are suitable only for those applications for which they were particularly designed. As a result, new NLO materials continually must be developed having properties selected for a particular application.

Furthermore, most known NLO materials have incongruent melting points. This means that as the compounds melt, the solid compound cannot coexist with the liquid of the same composition. The practical result is that the solid-to-liquid phase

transformation does not occur at a specific temperature for the entire material. Instead, the solid-to-liquid transformation occurs over a temperature range.

Among known NLO crystals, borates of the type LiB_3O_5 and BaB_2O_4 have found wide commercial success because of their capabilities for generating high-power laser light. LiB_3O_5 crystals have been used in patented devices. For example, Chuangtian et al.'s U.S. Pat. No. 4,863,283 describes an NLO device that uses a single LiB_3O_5 crystal. LiB_3O_5, for example, exhibits an insufficient birefringence to allow direct second-harmonic generation of UV light. Thus, applications using LiB_3O_5 generally have been limited to selected wavelengths. In contrast BaB_2O_4 exhibits a birefringence that is too high for most UV applications, complicating the optical set up that is required to achieve efficient operation in a system. The material $CsLiB_6O_{10}$ has an intermediate birefringence to that of LiB_3O_5 and BaB_2O_4 and it is well suited for high-power UV generation. Unfortunately, it is an extremely hygroscopic material that is difficult to manufacture; as a result, it has achieved only limited commercial success. The material $Sr_2Be_2(BO_3)_2O$ is another borate crystal that has been promoted for generation of short-wavelength light. To date, crystals of this material have not been grown with sufficient size and purity to demonstrate commercial viability.

Previous materials having the general formula $MSc_3(BO_3)_4$ crystallize in the space groups Cc, C2/c, or C2. These latter groups commonly have been associated with the laser material $Nd{:}LaSc_3(BO_3)_4$. See, Li, Yunkui; Aka, G.; Kahn-Harari, A.; Vivien, D. Phase transition, growth, and optical properties of $Nd_xLa_{1-x}Sc_3(BO_3)_4$ crystals *J. Mater. Res.* **2001**, *16*, 38-44. Despite numerous studies in the literature concerning $Nd{:}LaSc_3(BO_3)_4$, there apparently has been no previous consideration of the use of these materials for nonlinear optical applications involving the production of UV and VUV light. The literature primarily has addressed the use of $Nd{:}LaSc_3(BO_3)_4$ as a laser material.

Known NLO compounds are limited in their application to generation of UV and VUV light, are damaged by exposure to high-power lasers, exhibit excessive

absorption and light scattering of incident or absorbed light, and are too costly and time consuming for commercial production.

SUMMARY

The present disclosure concerns a nonlinear optical material according to Formula 1.

$$M_xM'_ySc_z(BO_3)_4$$

With respect to Formula 1, M and M' are rare earth metals, and the sum of x, y, and z is about four.

A second embodiment of the present disclosure includes a material according to Formula 2.

$$La_xM_ySc_z(BO_3)_4 \qquad \text{Formula 2}$$

With respect to Formula 2, x, y, and z are each greater than zero, the sum of x, y and z is about four, and M is selected from the group consisting of Y, Lu, Yb, and combinations thereof.

A third embodiment of the present disclosure includes a material according to Formula 3.

$$La_{1-x}Y_xSc_3(BO_3)_4 \qquad \text{Formula 3}$$

With respect to Formula 3, x is greater than zero and less than or equal to one. Typically x is from about 0.20 to about 0.3, and in a particular working embodiment, x was about 0.25.

Compositions comprising a nonlinear optical material according to the Formulas recited above are particularly useful for nonlinear optical applications. Such compositions can include, for example, a first nonlinear optical material according to Formula 1 joined to a second material, such as a laser material. In another embodiment, a composition can include a first material according to Formula 1, a second nonlinear

optical material, and a laser material. The compositions can be formed by joining materials by a method such as diffusion bonding or other suitable method.

Further embodiments of the disclosure concern devices that employ nonlinear optical materials. One such device is, without limitation, an optical parametric oscillator (OPO). An OPO uses NLO materials to produce widely tunable coherent light. Optical devices of the present invention comprise a light source, such as a laser, optically coupled to nonlinear optical materials that satisfy Formula 1, Formula 2 or both. Such devices may be used to generate UV light, VUV light or both.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a structural drawing of a compound having the formula $M_xM'_ySc_z(BO_3)_4$.

DETAILED DESCRIPTION

Disclosed embodiments of the present NLO material falls into the general class of compounds denoted by the formula $M_xM'_ySc_z(BO_3)_4$, where M and M' are rare earth metals. Typically, the rare earth metals are defined as including the lanthanides (elements 57-71), scandium and yttrium. In particular embodiments M and M' are selected from the group consisting of Y, La, Pr, Lu. Structural variations are observed for this family, depending on the identity of the of rare earth metals selected.

Materials suitable for NLO applications typically have a preferred structural adaptation that characterized by crystallization in the space group R32. As a result, claimed compounds include those of the formula $M_xM'_ySc_z(BO_3)_4$ crystallized in the R32 space group. A particular example of such a compound includes $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$ crystallized in the R32 space group.

Up to now, the stabilization and growth of a widely transparent R32 form of the general formula $M_xM'_ySc_z(BO_3)_4$ has not been demonstrated. The compound $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$ appears to represent the first such example of such a compound. It

is unique among all of the $MSc_3(BO_3)_4$ compounds in that it forms as a mixture of two rare earth metal atoms, La and Y, at a fixed composition ratio – La:Y – of about 3:1. The composition is essentially a line phase; meaning it is a distinct new compound. The results of an X-ray diffraction study of the material, which establishes the structure of the compound, are summarized in Tables 1 and 2.

Additional compounds according to the general formula, $M_xM'_ySc_z(BO_3)_4$ (Formula 1) that are useful as NLO materials can be selected from the group consisting of those having M and M' independently selected from the group consisting of La, Y, Lu, Yb, and Pr. One example is a compound according to the formula $Pr_{1-x}Y_xSc_3(BO_3)_4$. A second example is a compound according to the formula $Pr_{1-x}La_xSc_3(BO_3)_4$. A third example is $Lu_{1-x}Y_xSc_3(BO_3)_4$.

Table 1
Crystallographic data for $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$.

Parameter	Value/Property
Formula Weight, amu	496.51
Crystal System	Rhombohedral
Space Group	R32(h) [155]
a, Å	9.805(3)
c, Å	7.980(2)
V, $Å^3$	664.4(2)
Z	3
D_{calc}, g cm^{-3}	3.722
F(000)	695
Diffractometer	Rigaku AFC6R
Radiation	Mo Kα (λ=0.71069) graphite-monochromated
Data Collection	±h, k, ±l
No. Observations (total, unique)	2065, 380
$(F_o^2 \geq 3\sigma(F_o^2))$	380
R	0.022
R_w	0.031
Maximum Shift in Final Cycle	0.00
GOF	1.07

$R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o| = 0.022$
$R_w = [(\Sigma \, w \, (|F_o| - |F_c|)^2 / \Sigma \, w \, F_o^2)]^{1/2} = 0.031$

Table 2
Positional and thermal parameters (B_{eq}) and occupancy for $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$.

Atom	Wy	x	y	z	B_{eq}[a]
La[b]	3a	0	0	0	0.79(1)
Sc	9d	0.4572	0	0	0.56(2)
B(1)	3b	0	0	½	0.67(8)
B(2)	9e	0.5507(5)	0	½	0.72(6)
O(1)	9e	0.1405(4)	0	½	0.80(4)
O(2)	18f	0.5449(4)	0.8580(4)	0.4853(4)	1.16(4)
O(3)	9e	0.4081(5)	0	½	1.53(7)

[a] $B_{eq} = (8\pi/3)^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$
[b] occupancy = 0.154/0.1667, remainder of site is occupied by Y as demonstrated by electron microprobe analysis

The nonlinear signal of $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$ is approximately 0.67 times that of the NLO material BaB_2O_4. Furthermore, the high birefringence of the material provides a means for angular phase matching to produce UV and VUV wavelengths, in addition to broadly tunable radiation of both short and long wavelengths in OPO wavelengths. Thus, materials having the general formula $M_xM'_ySc_z(BO_3)_4$, particularly $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$ exhibit all of the characteristics in terms of optical and physical properties, as well as stability and manufacturability, that are necessary for a commercially successful NLO material.

Applications of Nonlinear Optical Materials

Devices using nonlinear optical materials may be manufactured. Such devices can be used, without limitation, for direct second-harmonic frequency conversion of laser light to visible, UV, and VUV wavelengths. Further uses of nonlinear optical materials in devices include frequency mixing, including sum and difference frequency mixing of laser light to yield light having a wavelength selected from the group consisting of infrared, visible, UV, and VUV wavelengths.

A further application of the current nonlinear optical materials uses the materials in a system, such as a monoblock laser system. Systems can be fabricated using a composite containing the current nonlinear optical materials. Such composites can contain a first material according to Formula 1, and a second material. The first material and the second material can be diffusion bonded or joined by another suitable method. Where the second material is a laser material, the nonlinear optical material can be oriented for angular phase matching and generation of the second harmonic of the laser.

A second system that can exploit nonlinear optical materials can be fabricated using two nonlinear optical materials and a laser material. The nonlinear optical materials can be the same or different materials, and one or both can be selected from

crystals having the general formula according to Formula 1. A first nonlinear optical material can be joined to a laser material by diffusion bonding, or other suitable method, and the nonlinear material can be oriented for angular phase matching of the second harmonic of the laser. A second nonlinear optical material can be joined to the first by a similar suitable method, such as diffusion bonding. The second nonlinear optical crystal can be oriented to yield, in conjunction with the first material, the fourth harmonic of the laser.

General Method for Making NLO Materials

A number of techniques, currently known or hereinafter developed, can be used to synthesize compounds that satisfy Formulas 1, 2 and 3. In general, and without limitation, compounds satisfying the general formulas have been synthesized by heating appropriate molar amounts of starting materials to a temperature sufficient to form the nonlinear optical materials. First, a mixture was formed comprising appropriate molar amounts of the various elements. The mixture was then heated to a temperature sufficient to form a single-phase mixture. Crystals were then allowed to grow from this stoichiometric melt. Transparent crystals of nonlinear optical materials were obtained by this process.

Working Examples

The following examples describe particular embodiments concerning the nonlinear optical material. These examples should be interpreted as illustrative with respect to certain embodiments only, and not to limit the invention to the specific features detailed therein. Thus, it should be understood that additional embodiments not limited to these particular features described are consistent with the following examples.

Example 1

This example describes the synthesis of $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$. Lanthanum oxide ($La_2O$, 0.8993 g, dried overnight in drying oven), scandium oxide (Sc_2O_3, 1.4683 g), yttrium oxide (Y_2O_3, 0.5343 g) and boron oxide (B_2O_3, 1.0981 g) were ground in a mortar and pestle. $LiBO_2$ (.8 g) was added and the mixture ground for 5 minutes. The ground material was transferred to a platinum crucible, covered, and heated in a furnace at 1 °C per minute, to 1050 °C. The material was held at this temperature for 2h, and then allowed to cool at 0.1 °C per minute. The material was then removed from the furnace and allowed to cool to room temperature. Several plate-like crystals were fractured from the material for X-ray crystallographic analysis.

Example 2

This example describes how the nonlinear optical materials described above can be used to generate second harmonic light energy. A Nd:YAG laser is used as a light source to generate 1064-nm light. This light is filtered and passed through a sample of NLO material prepared according to Example 1 and mounted on a silica glass plate. Second harmonic light energy emerges from the NLO crystal and is directed onto a photomultiplier tube to a dichroic mirror. The light energy may thereafter be monitored by an oscilloscope, such as purchased from Tektronix.

Appendix

The following references describe materials useful for optical applications, and applications of such materials. Each of the following documents are incorporated herein by reference:

Lin, ZhouBin; Hu, ZuShu; Han, XiuMei; Zhang, LiZhen; Wang, GuoFu. **Spectral parameters of Nd3+ ion in λ-Nd3+: LaSc3(BO3)4 crystal.** Physica Status Solidi B: Basic Research (2002), 231(2), 607-612.

Sardar, Dhiraj K.; French, Joe A.; Castano, Francisco; Sayka, Anthony; Salinas, Felipe S. **Temperature effects on the 1.0 and 1.3 μm emission lines of Nd3+ in a LaSc3(BO3)4 crystal host.** Journal of Applied Physics (2002), 91(12), 9629-9634.

Danailov, M. B.; Demidovich, A. A.; Kuzmin, A. N.; Kuzmin, O. V.; Hait, V. L. **On the performance of short pulse Nd3+:LSB microchip lasers.** Applied Physics B: Lasers and Optics (2001), 73(7), 671-676.

Sardar, Dhiraj K.; Castano, Francisco; French, Joey A.; Gruber, John B.; Reynolds, Thomas A.; Alekel, Theodore; Keszler, Douglas A.; Clark, Benjamin L. **Spectroscopic and laser properties of Nd3+ in LaSc3(BO3)4 host.** Journal of Applied Physics (2001), 90(10), 4997-5001.

Lin, Zhou-Bin; Hu, Zu-Shu; Wang, Guo-Fu. **Growth and characterization of γ-Nd3+:LaSc3(BO3)4 crystal.** Jiegou Huaxue (2001), 20(4), 256-258.

Li, Yunkui; Aka, G.; Kahn-Harari, A.; Vivien, D. **Phase transition, growth, and optical properties of NdxLa1-xSc3(BO3)4 crystals.** Journal of Materials Research (2001), 16(1), 38-44.

Kuz'micheva, G. M.; Rybakov, V. B.; Kutovoi, S. A.; Kuz'min, O. V.; Panyutin, V. L. **Morphotropic series of LnSc3(BO3)4 compounds.** Kristallografiya (2000), 45(6), 990-995.

Wang, Guofu; Chen, Wenzhi; Lin, Zhoubin; He, Meiyun; Hu, Zushu. **Neodymium-doped low-temperature phase lanthanum scandium borate self-frequency doubling laser crystal.**

Faming Zhuanli Shenqing Gongkai Shuomingshu (2000) Demidovich, A. A.; Kuz'min, A. N.; Kuz'min, O. V.; Ryabtsev, G. I.; Strenk, W. **Laser characteristics of Nd:LSB-KTP microchip under laser diode pumping.**

Lietuvos Fizikos Zurnalas (1999), 39(4-5), 381-384. Lebedev, V. A.; Pisarenko, V. F.; Selina, N. V.; Perfilin, A. A.; Brik, M. G. **Spectroscopic and luminescent properties of Yb,Er:LaSc3(BO3)4 crystals.** Optical Materials (Amsterdam) (2000), 14(2), 121-126.

He, Meiyun; Wang, Guofu; Lin, Zhoubin; Chen, Wenzhi; Lu, Shaofang; Wu, Qiangjin. **Structure of medium temperature phase β-LaSc3(BO3)4 crystal.** Materials Research Innovations (1999), 2(6), 345-348.

Goryunov, A. V.; Kuz'micheva, G. M.; Mukhin, B. V.; Zharikov, E. V.; Ageev, A. Yu.; Kutovoi, S. A.; Kuz'min, O. V. **X-ray diffraction study of the crystals $LaSc_3(BO_3)_4$ activated with chromium and neodymium ions.** Zhurnal Neorganicheskoi Khimii (1996), 41(10), 1605-1611.

The present invention has been described with reference to preferred embodiments. Other embodiments of the invention will be apparent to those of ordinary skill in the art from a consideration of this specification, or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

WE CLAIM:

1. A nonlinear optical material according to the formula $La_xM_ySc_z(BO_3)_4$, where x, y, and z are greater than 0, and M is selected from the group consisting Y, Lu, Yb, and combinations thereof.

2. The nonlinear optical material according to claim 1 where x is from about 0.7 to about 0.8.

3. The nonlinear optical material according to claim 1 where the material crystallizes in the space group R32.

4. A nonlinear optical material according to the formula $La_{1-x}Y_xSc_3(BO_3)_4$, where x is from about 0.2 to about 0.3.

5. A nonlinear optical material, comprising: $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$.

6. A nonlinear optical composition, comprising:

a first material according to the formula $M_xM'_ySc_z(BO_3)_4$, where M and M' independently are selected from the group consisting of the rare earth metals, x, y, and z are greater than zero, and the sum of x, y, and z is about four;

a second material joined to the first material.

7. The composition according to claim 6 where the second material is a laser material.

8. The composition according to claim 6 where the first material is $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$.

9. A device for generating high energy UV light, comprising:

a laser and a nonlinear optical material having the formula $La_xM_ySc_z(BO_3)_4$, where x, y, and z are greater than 0, and M is selected from the group consisting Y, Lu, Yb, and combinations thereof.

BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION

ABSTRACT

Novel nonlinear optical materials according to the general formula $La_xM_ySc_z(BO_3)_4$ have been prepared. Exemplary crystalline materials according to the general formula exhibit useful optical characteristics and desirable physical properties for nonlinear optical applications. Novel compositions and devices using the nonlinear optical materials also are described.

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For BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION
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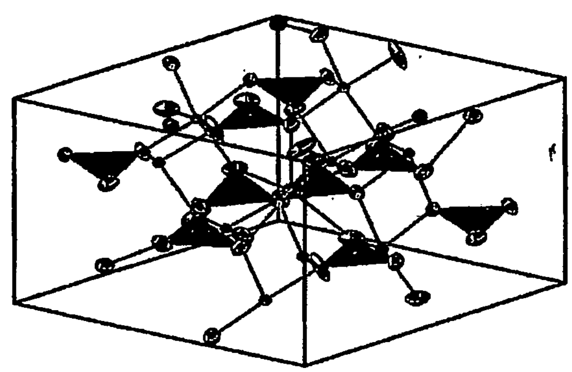

FIG. 1